

PATENT SPECIFICATION

(11) 1339910

1339910

DRAWINGS ATTACHED

- (21) Application No. 10957/71 (22) Filed 23 April 1971
 (31) Convention Application No. 36798 (32) Filed 13 May 1970 in
 (33) United States of America (US)
 (44) Complete Specification published 5 Dec. 1973
 (51) International Classification C23C 15/00
 (52) Index at acceptance

C7F 1V1 1V2 2A 2F 2M 2P 2W 2Z1 3C 4W 6A3
 6D1AX 6D3B 6F2



(54) ALLOY DEPOSITION BY LIQUID PHASE SPUTTERING

(71) We, UNITED AIRCRAFT CORPORATION, a corporation organized and existing under the laws of the State of Delaware, United States of America of 400 5 Main Street, East Hartford, Connecticut, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates in general to the field of metals and alloys and, more particularly, to the formation or deposition 15 of alloy coatings in sputtering processes.

The generation of metal deposits and apparatus therefor are recognized in the art as, for example, in the United States patents to Moseson 3,305,473 and 3,393,142 and 20 that to Rausch 3,458,426. Sputtering is generally considered to involve the solid state sublimation of a target material caused by ion impact on its surface. The sublimed material forms a unique high energy atomic beam which is ideally suited to the preparation of metal or alloy films and coatings which are characterized by excellent adherence to the coating substrate and an exceptionally fine grain structure.

30 The major drawback to the conventional sputtering process is its low deposition rate, nominally about 500 Angstroms per minute, in a diode configuration. These low rates are not constant with the generation of 35 coatings in the thicknesses usually required, as for example on gas turbine engine parts for oxidation resistance, or in the production of alloy deposits in bulk product dimensions.

40 Recently new coatings have been developed for providing dramatic improvements in the operating lifetimes of components exposed to dynamic oxidizing environments at very high temperatures. They are currently applied 45 by thermal evaporation techniques. However, these new coating alloys have chemistries of relative complexity and thermal vaporiza-

tion, in all but a few special cases, causes fractionation of an alloy into its constituent parts, the more volatile constituents being vaporized first, thus rendering the deposits from the vapor heterogeneous in composition. To obtain a deposit of homogeneous character over an extended time period requires that the evaporation liquid composition be adjusted and continually modified by a feed of appropriate solid to correct for the fractionation tendency.

The sputtering techniques substantially reduce the fractionation tendency of alloys because atoms removed by sputtering escape without relation to their natural vaporization tendency and, therefore, the sputtered vapor composition is primarily dependent upon the proportion of alloying elements at the sputtered surface and the fraction of sputtered atoms in the total vapor at any given time.

This invention pertains to an improved sputtering process characterized by a high rate of deposition. It pertains to methods for depositing alloys or coating objects of uniform chemical composition by the condensation of vapor sputtered from a liquid alloy surface.

The drawing is a schematic of the apparatus utilized for sputtering from liquid phase targets.

The preferred system for effecting deposition on a substrate 14 by condensation of vapor sputtered from a liquid alloy target is diagrammed schematically in the drawing. A vacuum chamber 1 with suitable valves and pumps and insulated feed-throughs is exhausted through port 2 against a controlled argon leak admitted through opening 3 to maintain a dynamic pressure of $1-5 \times 10^{-3}$ torr. A water cooled copper hearth 4 containing the alloy target charge 5 and electrically insulated from the chamber by dielectric sleeve 6, is connected to a controlled power supply 7 and negatively biased. A shield 8 is positioned symmetrically around the hearth on the inside of the chamber so that only the liquid target surface is allowed to sputter. An

50

55

60

65

70

75

80

85

90

BEST AVAILABLE COPY

electrically heated thermionic emission filament 9, insulated from the chamber, is placed about one centimeter above the liquid level in the hearth and is powered by an alternating current power supply 10. A bias of 60—100 volts is imposed on the filament by a regulated direct current power source 11, causing a glow discharge to form between the filament 9 and all objects at ground potential, including the chamber, provided that the filament is at its operating temperature of about 1371°C (2500°K). A discharge current of about 0.79—2.36 per square cm (2—6 amperes per square inch) of hearth surface is required, which area in the described apparatus was 15.9 cm (6.25 inches).

An adjustable magnetic field of 1—200 Gauss, aligned to provide its field axis normal to the liquid target surface, is produced by a solenoid 12 powered by a direct current power supply 13. The magnetic field increases the degree of ionization in the discharge, and as the negative bias of the hearth is increased the charge is melted by an intense ion bombardment. As the alloy target passes into the liquid phase a substantial and unexpected current increase from power supply 7 occurs which causes rapid sputtering of the liquid surface and allows the thermionic filament temperature to be reduced or, in some cases, allows the filament current to be shut off. Thermionic and other unknown electron emission mechanisms provide the electrons necessary to support the glow discharge formerly supplied by the filament. Thus, in a regime of the diode type, sputtering occurs when the target is molten and at a thermionic emission temperature.

In one case, an alloy having a nominal composition, by weight, of 25 percent chromium, 6 percent aluminium, 0.1 percent yttrium, balance iron, was liquified and deposited by condensation on a substrate. The deposit analyzed at, by weight, 31 percent chromium, 4 percent aluminium, 0.1 percent yttrium, balance iron. In this particular case a power density of 130 watts per square centimeter of liquid target surface was used at a hearth potential of 2600 volts. The total power input was 9.9 kilowatts for 180 minutes during which time 120 grams of a total charge of 250 grams was removed from the target. A coating deposition rate of 254μ (10 mils) per hour was experienced at a distance of 8.9 cm (3.5 inches).

In the case of an iron-30 percent vanadium alloy, which would yield a theoretical deposit with a calculated analysis of 0.02 percent vanadium by thermal evaporation, revealed a deposit of 10.3 percent vanadium, balance iron, or better than 500 times the predicted value for vanadium by thermal evaporation alone. The iron-vanadium target was sputtered at 105 watts per square centimeter of

melt surface with a total system power of 6.3 kilowatts for a period of 225 minutes, in which time 93 grams of a 315 gram target were removed. The deposition rate was 68.5μ (2.7 mils) per hour at a substrate separation of 8.9 cm (3.5 inches).

The process was also investigated in the case of elemental tin which has a conveniently low melting point and a very low vapor pressure such that virtually no thermally induced vapor would be obtained from the liquid target. A comparison of the respective sputtering rates of liquid and solid tin targets at specific bombarding energies revealed that the yield from the liquid target was up to 15 percent higher than that for the conventional solid target.

There is, of course, inherent in this process a combination of two effects, sputtering of the liquid surface and thermal evaporation. It has been established, however, that sputtering can exert a significant beneficial effect on the composition of the vapor and, in systems where constituent vapor pressures are low, predominates as the method for vapor production. The method has also been demonstrated to provide exceptionally high sputtering rates and the capability for retaining to a large degree the chemical integrity of the target composition in the deposited material.

The very high sputtering rates achievable from liquid phase are thought to occur for the following reasons:

1. Atoms are released more readily from the surface of a target as the temperature is increased.

2. Electron emission from the ion bombardment surface increases on liquefaction and contributes to a higher ion density in the gas phase over the liquid alloy helping to sustain the plasma. This is probably the primary reason why the use of the thermionic filament becomes unnecessary when a high temperature liquid is sputtered.

3. The high metal atom content in the vapor over the liquid itself provides a source of ions for self-sputtering by the atoms of the target material itself. Self-sputtering is an efficient process because the equal mass of the bombarding ion and the surface atom of the sputtering material is the most ideal case for momentum transfer. And it has been shown that, after startup, the system pressure can be reduced and the sputtering mechanism can be retained even in an ultrahigh vacuum regime.

Certain other features and advantages of the present method are provided for coating objects, such as turbine hardware, with complex alloys. First, the intense electron emission from the liquid pool undergoing ion bombardment is a useful source of heat for parts being coated, preheat of such parts often improving coating adherence and integrity.

70

75

80

85

90

95

100

105

110

115

120

125

130

BEST AVAILABLE COPY

- Secondly, the pressure range over which sputtering is conducted requires only mechanical pumps for the attainment of the desired vacuum conditions. Thirdly, the ion bombardment density is uniform over any desired surface area so that complex hearth shapes, conforming generally to the shape of the article to be coated, can be utilized for conservation of the target material. Thus, collection efficiencies of 25—50 percent have been obtained on substrates similar in size to the 6.35 × 6.35 cm (2.5 × 2.5 inch) hearth utilized in the program. Fourthly, because the size of the liquid pool can be large in relation to the size of the part being coated, shadowing effects on geometrically complex parts such as turbine blades are minimized.
- It is evident that in appropriate circumstances other suitable means of liquefaction of the target can be utilized and that sputtering from the liquid phase can occur as long as the biasing requirements are met. Also, any suitable gas such as argon or combinations of gases providing the required discharge density in the vicinity of the liquid pool can be utilized for sputtering. It is also evident that, if sufficient power density is provided at the liquid surface, ionization of the vapor atoms in the process of sputtering can provide the necessary ion bombardment for sustaining the deposition operation which would preclude the necessity for the use of a discharge gas altogether.
- Thus, the invention in its broader aspects is not limited to the specific steps, parameters, compositions, combinations and improvements described, but departures may be made therefrom within the scope of the appended claims.
- 40 WHAT WE CLAIM IS:—**
1. Process for forming an alloy coating on a metallic substrate comprising generating a glow discharge in a vacuum chamber between a metal charge and a filament arranged in the vacuum chamber; liquefying the metal charge composed of the constituent elements of the alloy by means of the glow discharge: biasing the metal charge at a controlled negative voltage: forming a homogeneous vapor cloud of the alloy in the chamber by sputtering from the surface of the liquefied charge and condensing the vapor on the surface of the substrate.
 2. A process according to claim 1, wherein the constituent elements of the alloy have diverse vapor pressures at the temperature of the liquefied charge.
 3. Apparatus for liquefying and sputtering alloys which comprise a vacuum chamber having access means for evacuation of the chamber and admission of a controlled gas leak; a hearth in the chamber to receive a metal charge to be sputtered with its sputtering surface oriented horizontally, the hearth being configured at its upper end to contain a liquid in electrical isolation from the chamber a filament arranged above the sputtering surface of the metal charge and adapted to cause a glow discharge to be established between the metal charge and the filament to cause sputtering of the metal charge, means for biasing the metal charge positioned in the hearth at controlled negative voltage; an emission shield surrounding the hearth, substantially shielding the hearth from ion bombardment, the shield having an upwardly directed opening defining an alloy surface area to be sputtered; means insulated from the chamber for melting at least a portion of the target; means for producing in the metal charge in the hearth a magnetic field normal to the upper surface of the charge and means for mounting a deposition substrate above said opening in the hearth.
 4. Apparatus according to claim 3, in which the means for melting the metal charge comprises an electrically heated alternating current thermionic emission filament, insulated from the chamber and positioned immediately adjacent and horizontally across the upper end of the hearth for melting the alloy target, the filament allowing the passage of sputtered ions thereby.
 5. A process for forming an alloy coating on a metallic substrate substantially as hereinbefore described with reference to the drawing.
 6. An apparatus for liquefying and sputtering substantially as hereinbefore described with reference to the drawing.

W. SWINDELL & PEARSON,
Chartered Patent Agents,
44, Friar Gate, Derby.
and at Hanley.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1973.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.

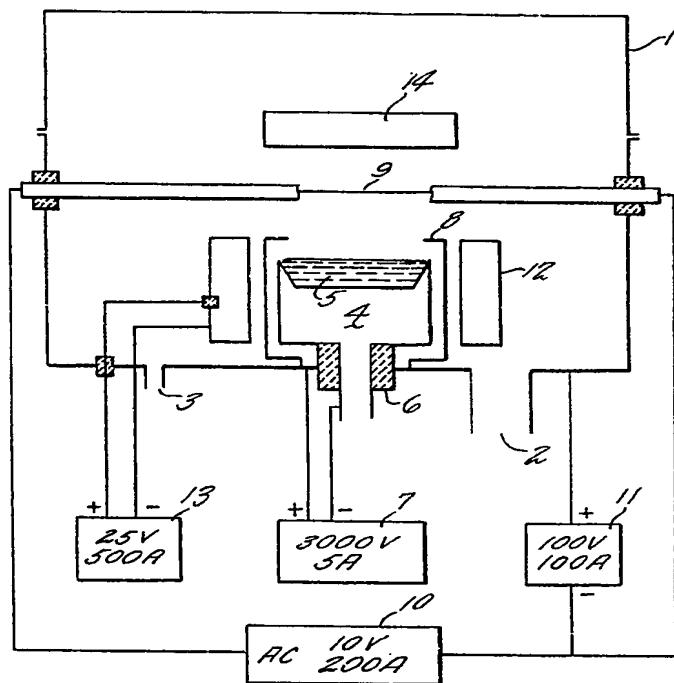
BEST AVAILABLE COPY

1339910

COMPLETE SPECIFICATION

1 SHEET

This drawing is a reproduction of
the Original on a reduced scale



BEST AVAILABLE COPY